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AN ELECTRON MICROPROBE STUDY OF INCLUSIONS IN LEAD TELLURIDE THERMOELECTRIC ELEMENTS

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ABSTRACT

An electron probe and metallographic examination was performed on a lead-tin telluride alloy doped with manganese dioxide in order to determine the chemical role of manganese and other constituents with respect to contacting and nonmetallic inclusions in the alloy. Analysis indicates that the three distinct types of minor phase inclusions which were observed are composed of mixed manganese oxides, tin, and graphite.

Elements bonded to an iron cup were also examined. Results show some diffusion of iron into the alloy but no evidence of an iron-tellurium reaction. No differences in microstructure or manganese distribution were detected between those elements which formed sound bonds and those which did not.

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INTRODUCTION

A recent development in the continuing efforts to improve the chemical and electrical stability of p-type lead telluride for thermoelectric applications has been the addition of tin and manganese. An example of this is the alloy of lead, tin, and telluride doped with manganese dioxide which is being marketed by the Minnesota Mining and Manufacturing Company under the trade designation TEGS-3P. The element fabrication method used for this material is a cold powder pressing and sintering process. As is well known, difficulties have been experienced in using p-type lead telluride for extended periods of time due to the fact that significant changes in its thermoelectric properties occur after some time at operating temperatures, particularly when iron contacts are used. Although its thermoelectric figure of merit is somewhat lower than that of previous p-type lead telluride materials, TEGS-3P is claimed to be considerably more stable and capable of stable operation at higher temperatures.

As yet, comparatively little is understood about the chemical role played by the manganese in stabilizing the material or about its effect on contact processes. Instances have been observed in which nucleation and growth of apparently nonmetallic inclusions have occurred in TEGS-3P material during prolonged storage under clean atmospheric conditions. Evidence of prior work indicates that these inclusions are associated in some manner with the presence of manganese. The work reported herein has been conducted in an attempt to determine decisively what chemical elements are associated with the inclusions both in undisturbed material and in the material near a bonded iron contact.

EXPERIMENTAL PROCEDURE

An examination of two different lots of TEGS-3P thermoelectric elements was carried out using electron microprobe analysis. The elements were approximately 1/2 inch in diameter and 1/2 inch

long, one of the largest element sizes for which the cold pressing and sintering method of fabrication has been attempted. The two element lots, which were supposedly identical, showed different responses to the contacting process. One element lot, designated 7B, formed sound, strong, low resistance bonded contacts to iron. The other lot, designated 2B, formed high resistance contacts which were physically very weak and which exhibited considerable over-reaction between the element and the bond material, resulting in an erosion of the element in the vicinity of the bond. The bonding process employed was identical for the two lots.

Five unbonded elements from each lot were examined by microprobe analysis. In addition, a bonded sample from each lot was examined with particular attention being paid to the region of the contact.

The instrument used for this study was the Applied Research Laboratories (ARL) Electron Microprobe X-Ray Analyzer (EMX). This instrument produces a stream of electrons which are focused by electromagnetic lenses on a spot approximately one micron in diameter at the surface of the specimen. As a result of the electron bombardment, X-rays characteristic of the elements present in the sample are produced and are detected and analyzed by means of three analyzing crystal spectrometers within the unit. All elements from boron (atomic number 5) to uranium (atomic number 92) can be detected with this unit. The X-ray signals produced can be read out by means of a strip chart recorder, a scaler, or an oscilloscope. In addition, backscattered electron and sample current signals can also be detected. The specimen can be moved along two axes manually and can be moved under the electron beam at a constant rate of 8 or 96 microns per minute. It can be observed visually during the entire analysis with an optical microscope incorporated in the unit. The X-ray signals from all three spectrometers can be sent to a three-pen recorder so that X-ray intensity can be plotted as a function of position (see Figures 10, 11 and 12). A line profile analysis can also be obtained. In this mode of operation the electron beam moves across the specimen in a horizontal or vertical path while the specific X-ray signal is sent to the oscilloscope. In this manner intensity is observed on the oscilloscope as a function of beam position (see Figures 7 and 15).

An electron beam scanning (EBS) system is incorporated into the EMX. In this mode the electron beam is made to scan the specimen both vertically and horziontally. The X-ray signal is sent to the oscilloscope, which is scanning in sequence with the electron beam, for display of its intensity as a function of beam position. If, for example, a spectrometer is set to detect a particular element and the signal is sent to the oscilloscope during the scanning mode, a two-dimensional pattern representing the distribution of that element within the specimen is obtained on the screen. Similar results can be obtained by sending the backscattered electron or sample current signals to the oscilloscope. As backscattered electron and sample current signals are a function of atomic number, these signals can give a general description of the surface of the specimen based on the distribution of the elements.

RESULTS AND DISCUSSION

The microprobe analysis was performed with the goal of answering the following questions:

1. What is the distribution of manganese in the "as received" material?

2. Can a chemical association between manganese and any other element in the material be demonstrated? (Of particular interest are oxygen, carbon and tellurium.)
3. It is possible to demonstrate any significant chemical differences between the two batches 2B and 7B, which reacted differently to the bonding process?

The evidence obtained relative to each of these questions is presented and discussed below.

Manganese Distribution and Included Phases

Visual microscopic examination of all specimens showed two apparently different types of metallic-appearing inclusions in the lead telluride matrix. Voids could also of course be distinguished (the TEGS-3P material being a powder product, is not fully dense), and also a few dark inclusions were observed whose visual appearance indicated that they were nonmetallic.

Figure 1, an electron backscatter picture, shows an example of the far more prevalent of the two metallic inclusions, hereafter referred to as the Type I inclusion. This picture is electrically biased toward the elements of high atomic number, so the low atomic number elements appear dark. Voids can also appear as dark areas. Figure 2 shows a manganese X-ray scan while Figure 3 shows a carbon X-ray scan of the same area. It is obvious that the distinctive pattern of the included phase in each photomicrograph is dark on the backscatter pattern (low atomic weight) and light on the manganese pattern, indicating that the Type I inclusions are high in manganese and contain no lead or tellurium. Figure 3 indicates that they also contain no carbon. Furthermore, the low level of manganese in the matrix, shown by the dark background in the manganese scan, indicates that the level of manganese present in the structure is far below that in the included phase. This condition was found in all samples analyzed and is therefore believed to be universally prevalent.

Figure 4 shows a backscatter presentation of the Type II metallic inclusion which appears light gray upon visual examination. The characteristic brightness of the inclusion in Figure 4 indicates that it is made up primarily of material whose atomic weight is lower than that of the matrix. Figure 5 shows a tin X-ray scan and Figure 6 a tellurium scan of the same inclusion. It can be seen that the inclusion is high in tin and low in tellurium. The conclusion is that the Type II inclusion is primary tin.

Figure 7 shows an example of the area where Type III nonmetallic inclusions were encountered (upper right quadrant) as well as some Type I inclusions (lower left quadrant). Figure 7 is a backscatter scan of this area with a manganese line profile trace superimposed on it. The vertical axis indicates the intensity of the X-ray and is related to the amount of manganese present. The line across the center of the specimen indicates the path of the electron beam on the sample. It can be seen that the amount of manganese varied considerably as the beam traversed the sample. This fact is verified by Figure 8 which is a manganese X-ray scan of this area. Figure 9 is a carbon X-ray scan indicating that the Type III inclusion (upper right quadrant) is rich in carbon and again that the manganese Type I inclusion contains little or no carbon.

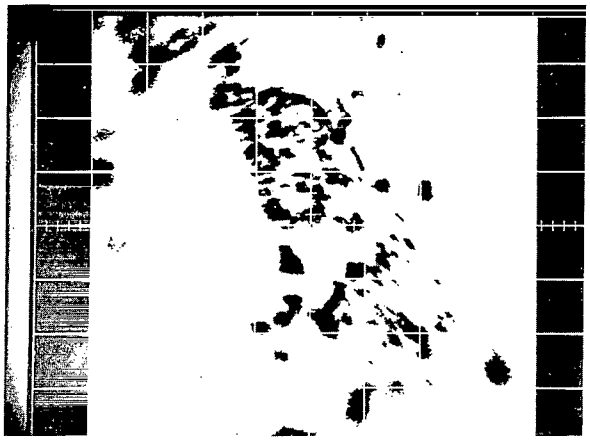

Figure 1. Backscatter pattern of Type I inclusion area, Sample 8 (2B), magnification 400X.

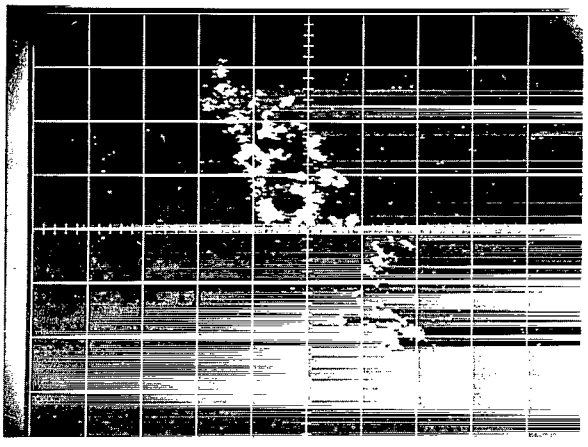

Figure 2. Manganese X-ray scan of Type I inclusion area, Sample 8 (2B), magnification 400X.

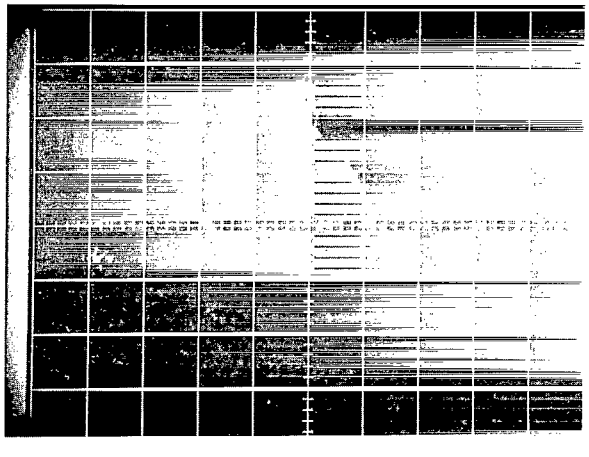

Figure 3. Carbon X-ray scan of Type I inclusion area, Sample 8 (2B), magnification 400X.

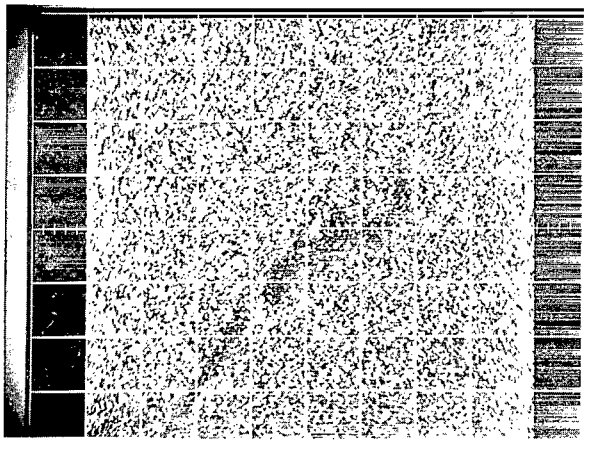

Figure 4. Backscatter pattern of Type II inclusion, Sample 10 (2B), magnification 1700X.

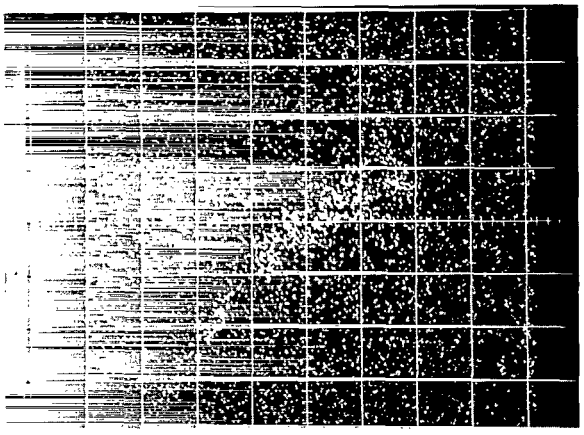

Figure 5. Tin X-ray scan of Type II inclusion, Sample 10 (2B), magnification 1700X.

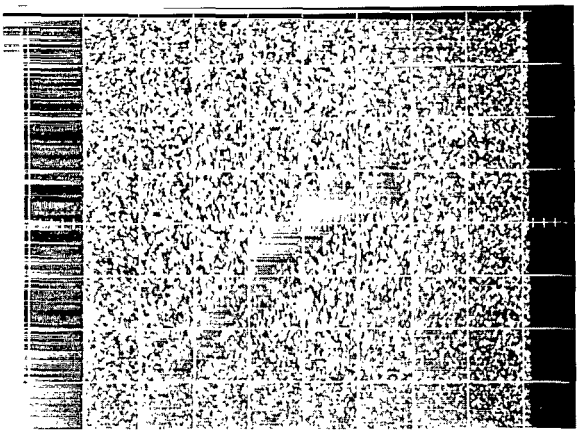

Figure 6. Tellurium X-ray scan of Type II inclusion, Sample 10 (2B), magnification 1700X.

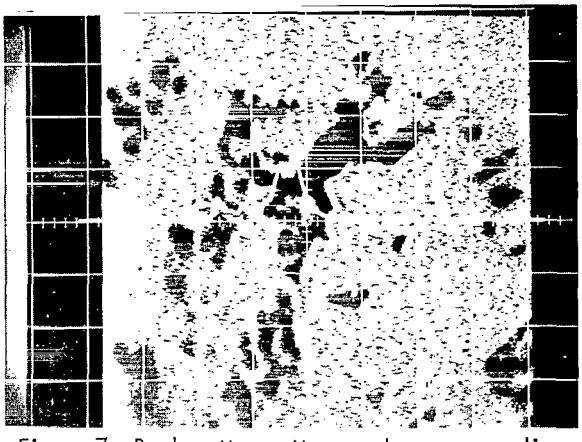

Figure 7. Backscatter pattern and manganese line profile trace of type III inclusion area, Sample 1 (7B), magnification 450X.

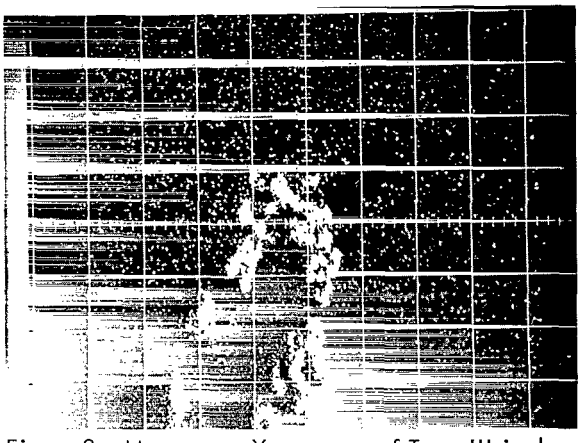

Figure 8. Manganese X-ray scan of Type III inclusion area, Sample 1 (7B), magnification 450X.

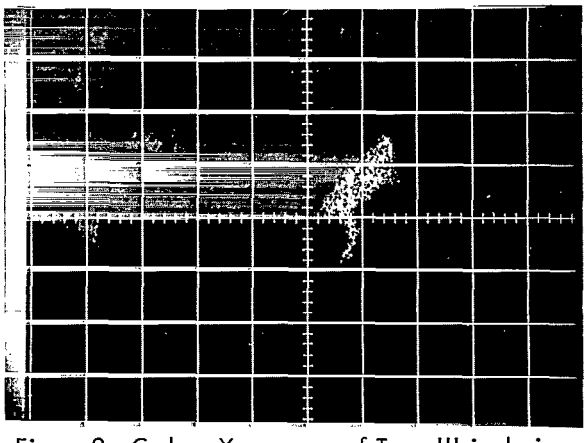

Figure 9. Carbon X-ray scan of Type III inclusion area, Sample 1 (7B), magnification 450X.

Chemical Associations with Manganese in the Type I Inclusions

Figure 10 shows a recorder plot of the intensity of manganese X-rays and oxygen X-rays obtained as the specimen moved under the beam at 8 microns per minute. The sample is specimen 4 (7B) which contains Type I inclusions. It is seen that the correlation between the concentration peaks of the two elements is quite good, with all areas which are higher in manganese also being high in oxygen. Figure 11 shows similar plots of manganese and carbon X-ray intensities across another area of the same sample with Type I inclusions. It can be seen that there is no correlation between the manganese and carbon concentrations. No rise in carbon concentration occurs in the vicinity of the manganese peaks, and the only significant rise in carbon concentration soon occurs at a point where the manganese concentration is slightly below that dissolved in the lead telluride. The conclusions drawn from these observations are that Type I inclusions consist of a manganese/oxygen compound and that no chemical association exists between manganese and carbon in TEGS-3P material. The direct correlation between manganese and oxygen concentrations is demonstrated even more graphically by Figure 12, which shows manganese and oxygen plots on sample 1 (7B) of the Type I inclusion area shown in Figure 13.

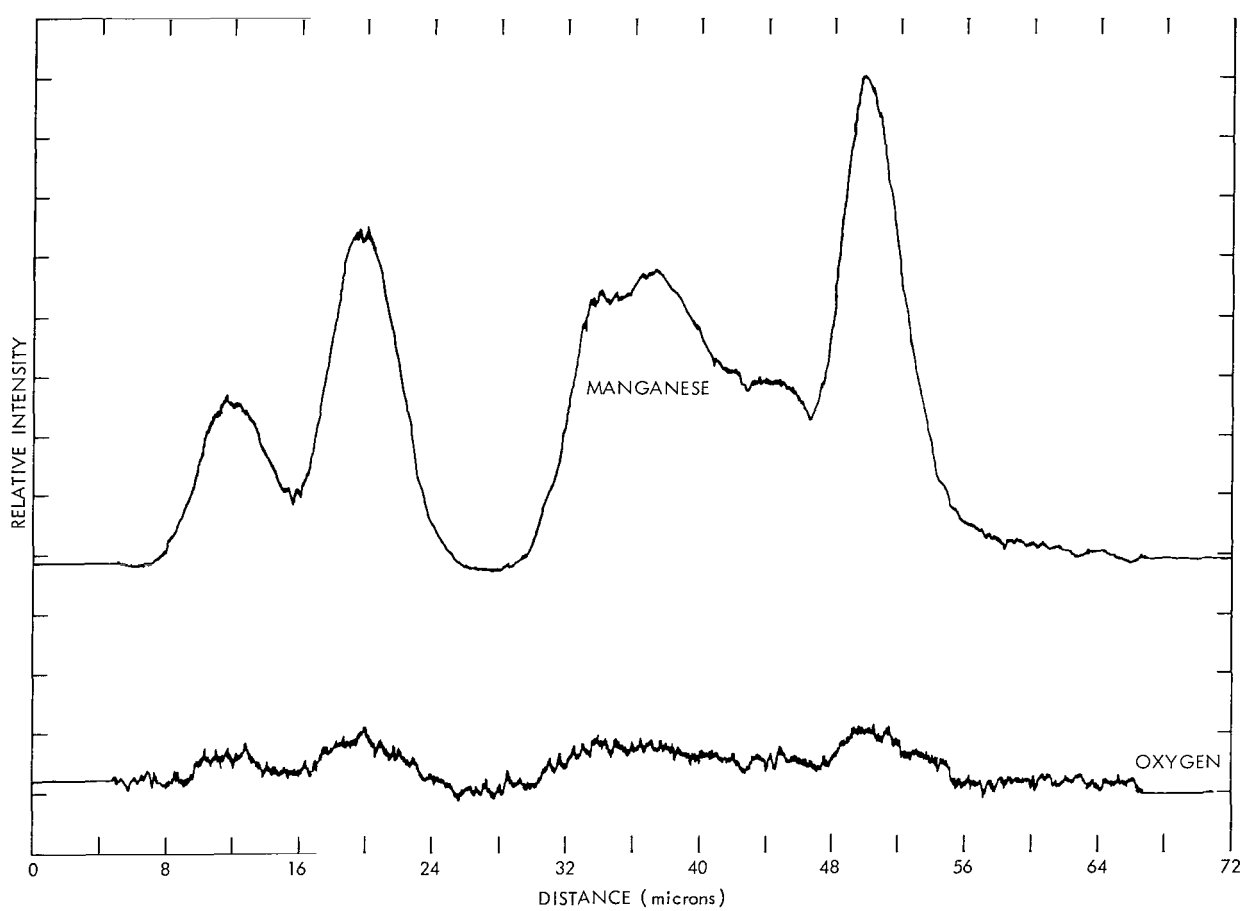

Figure 10. Intensity of manganese and oxygen X-rays as a Function of position across Sample 4 (7B), containing Type I inclusions.

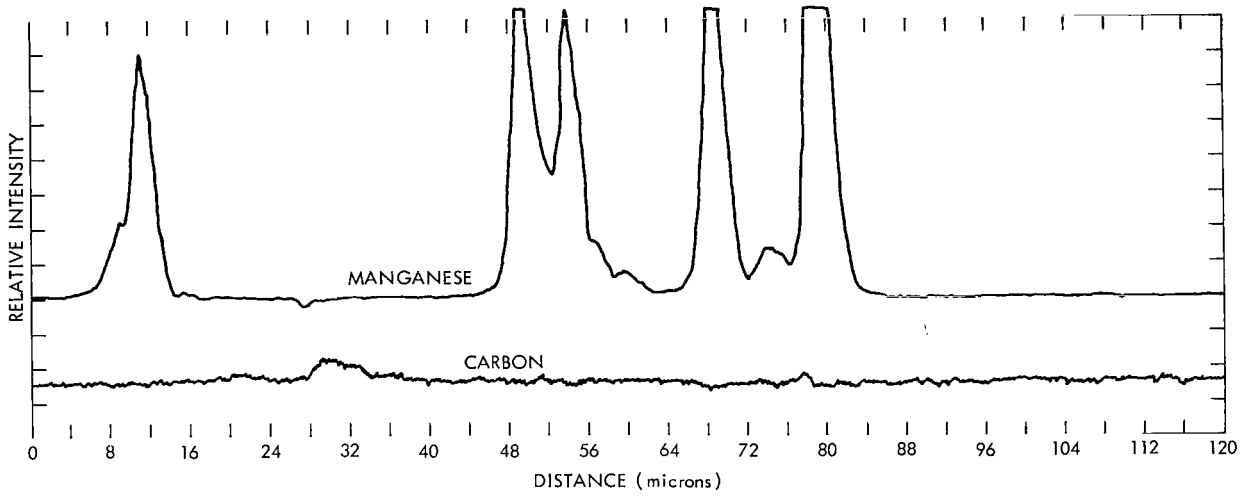

Figure 11. Intensity of manganese and Carbon X-rays as a Function of position across Sample 4 (7B), containing Type I inclusions.

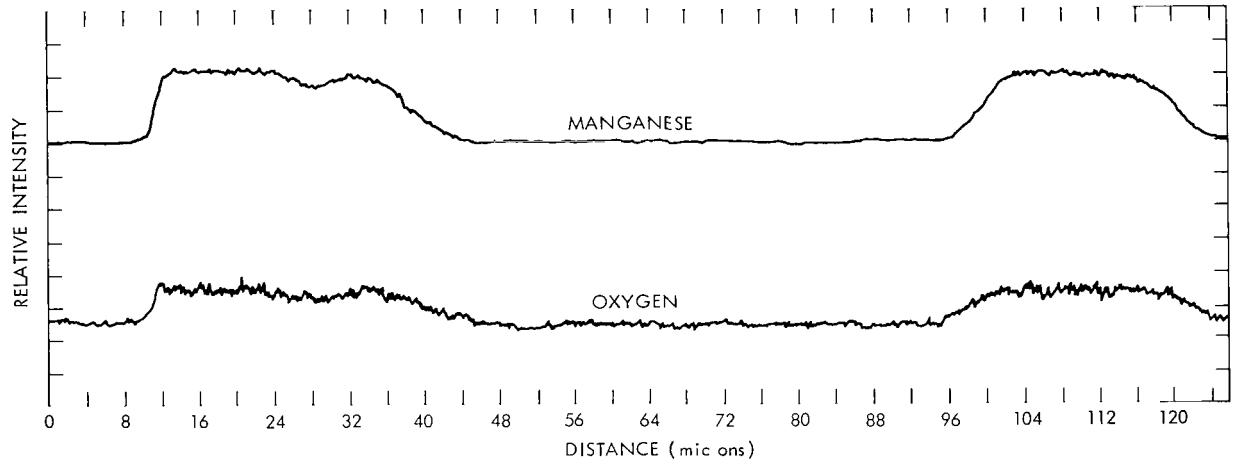

Figure 12. Intensity of manganese and Oxygen X-rays as a Function of position across Sample 1 (7B), containing Type I inclusions.

An attempt was made to determine the approximate manganese concentrations in the matrix material and in the Type I inclusions. Counts of manganese obtained from both phases were compared to the counts obtained from a pure manganese standard, with both the samples and the pure standard corrected for background, but not corrected for absorption or atomic number effects. Values of 1.43 percent manganese and 73.34 percent manganese were obtained for the matrix and the Type I inclusion respectively. The matrix value compares favorably with values of 1.346 to 1.390 percent previously obtained for the total manganese concentration in TEGS-3P material. (These previous measurements were made by both emission spectroscopy and activation analysis.) The value for the Type I inclusion lies between the theoretical values for MnO (77.45 percent Mn) and the next higher stable oxide of manganese Mn_3O_4 (72.03 percent Mn). This further supports the contention that the Type I inclusions are mixed manganese-oxygen compounds. Table 1

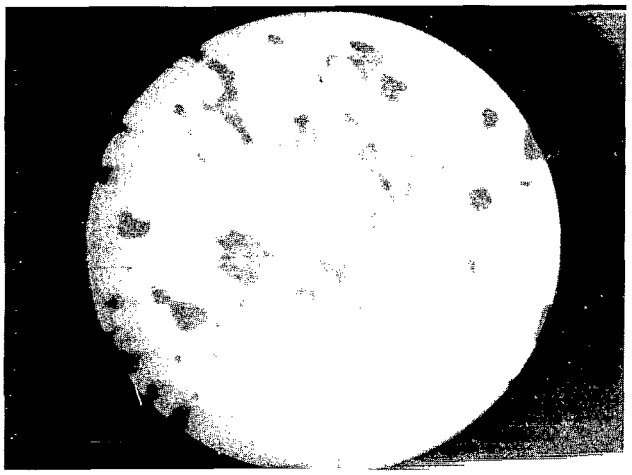

Figure 13. Photomicrograph of Type I inclusions, Sample 1 (7B), magnification 280X.

lists some of the characteristics of the known oxides of manganese. MnO_2 is a form of the natural ore of manganese and is the most stable oxide under near atmospheric conditions of temperature and pressure. The manganese concentration found in the Type I inclusions indicates that the average oxidation number of the manganese is lower than +4 which corresponds to MnO_2. Thus it would be anticipated that the Type I inclusions would slowly oxidize to the more stable MnO_2 form. A volume increase accompanies this gradual oxidation.

Table I

Oxide	Color	Melting Point, °C	Theoretical Weight, Percent Min.
MnO	gray-green	1650	77.45
Mn_3O_4	brown-black	1705	72.03
Mn_2O_3	brown-black	loses oxygen at 1080	69.60
MnO_2	black	loses oxygen at 230	63.19
MnO_3	red	decomposes	53.37
Mn_2O_7	red oil (hydroscopic)	-20	49.52

Comparison Between the Two Batches (7B and 2B)

Comparison of previous sets of Figures indicates that identical patterns exist in the 2B and 7B batches with regard to types of inclusions, their morphology, and their compositions. For example, Figures 1, 2, and 3 show a Type I inclusion in a 2B sample (No. 8) which is identical to the Type I inclusions shown in Figures 7, 8, and 9 in a 7B sample (No. 1). As previously stated this condition was found in all of the elements investigated. Examples of the Type II and Type III inclusions were also found with about equal frequency in samples of both batches, although the Type II inclusion (primary tin) was significantly less prevalent than the other inclusion types.

Analysis of Bond Area

Figure 14 shows a typical bond region with the components of the assembly and the divisions between them indicated at the periphery of the picture. Figure 15 shows a backscatter scan of

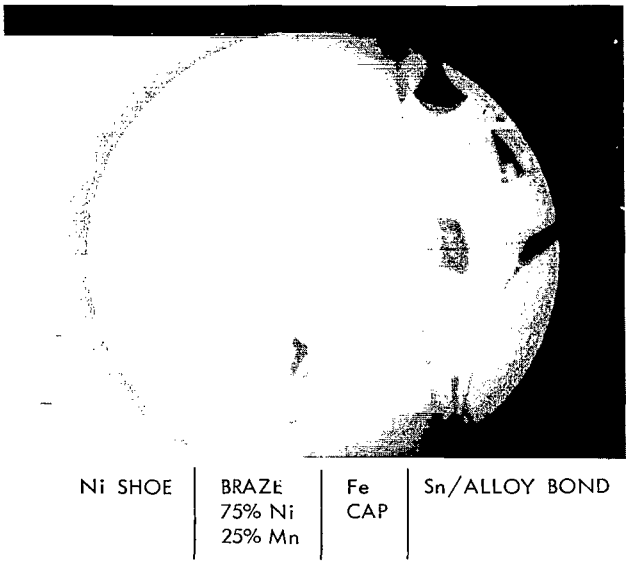

Figure 14. Photomicrograph of Typical bond region, Sample 1 (7B), magnification 280X.

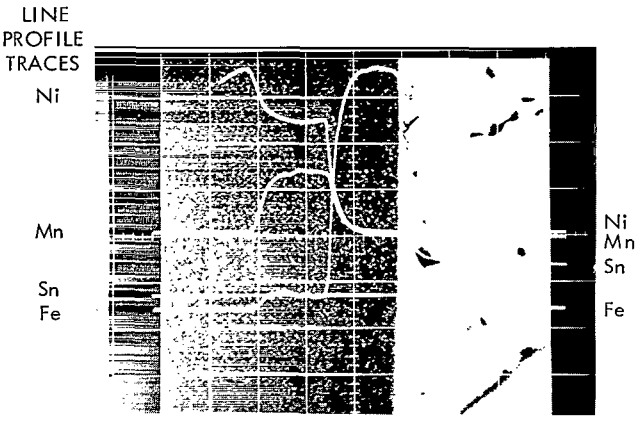

Figure 15. Backscatter pattern and line profile traces of bond region, Sample 1 (7B), magnification 280X.

the same region with line profile traces of iron, tin, manganese, and nickel superimposed on the picture (again the center line indicates the path of the beam). The peaks in the nickel, manganese and iron traces can be correlated exactly with the relative positions of the nickel shoe, 75 percent Ni, 23 percent Mn braze layer, iron cap, and tin alloy bond respectively. The tin trace peaks at the bond layer and then remains at a constant level due to the presence of tin as a constituent of the TEGS-3P material. The manganese trace peaks in the 75 percent Ni, 25 percent Mn braze layer and then drops to a constant level in the thermoelectric material. The absence of manganese peaks in the thermoelectric material indicates that no Type I inclusions were present in this region. The nickel trace drops to zero in the iron cap, indicating that no nickel penetrates the cap and reaches the thermoelectric element. Finally, the iron trace drops rapidly to zero in the thermoelectric material, indicating that the amount of diffusion of iron into the thermoelectric material is small but finite. This is further illustrated by Figure 16, an iron X-ray scan of the same bond region, which shows a small uniform penetration of iron into the thermoelectric element with no indication of iron telluride formation. It should be noted, however, that the element being examined here is in the "as bonded" condition. The distribution of the elements might be expected

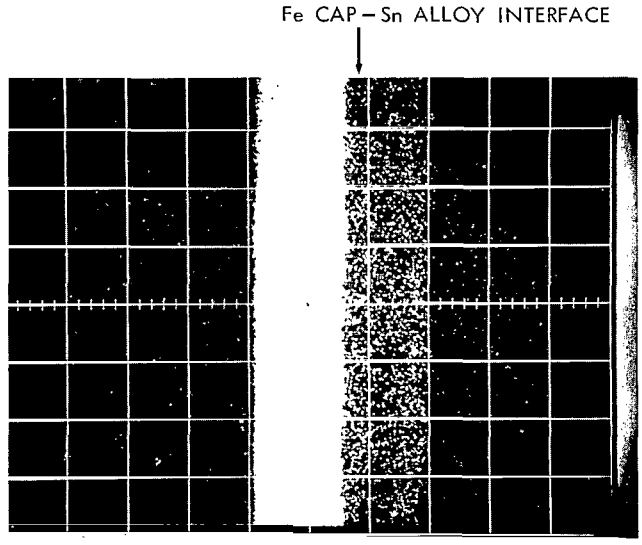

Figure 16. Iron X-ray scan of bond region, Sample 1 (7B), magnification 450X.

to change drastically by diffusion during prolonged operation of the juction at elevated temperatures.

CONCLUSIONS

These results have led to the following conclusions about the compositions and morphologies of phases existing in TEGS-3P thermoelectric material:

1. At least three distinct types of included minor phases exist in the material. These have been identified as:

   Type I - mixed manganese oxides

   Type II - elemental tin

   Type III - graphite

2. The manganese which is agglomerated in the Type I inclusions always has oxygen chemically associated with it and never has carbon associated with it. Its average oxidation number is less than +4 which corresponds to MnO_2. The remainder of the manganese present is uniformly dissolved in the lead telluride.

3. Elemental carbon (graphite) is found in the lead telluride matrix, sometimes physically associated with voids in the structure.

4. No detectable differences in composition or phase morphology exist between two batches of elements which reacted completely differently in the contacting process.

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National Aeronautics and Space Center
Greenbelt, Maryland, April 11, 1969
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